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(54) HARDNESS INSENSITIVE DETERGENT COMPOSITION

(71) We, THE PROCTER & GAMBLE COMPANY, a Company organised under the laws of the State of Ohio, United States of America, of 301 East Sixth Street, Cincinnati, Ohio 45202, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to novel cleansing and laundering compositions having minimal potential effect on the environment. More particularly, it relates to detergent compositions containing a calcium insensitive detergent material and a citrate compound which provides superior levels of cleaning and whitening heretofore unobtainable without employing the conventional surfactants and phosphate builder salts. A preferred embodiment of the invention is the use of the calcium insensitive detergent material and the citrate builder compound with a proteolytic enzyme.

It is known that when builders are added to the active synthetic detergent component or components of washing compositions, an increase in cleaning ability or whiteness maintenance or both is obtained even though the washing solution may contain less of the active detergent.

The use of enzyme in admixture with detergent compositions is also known and is described, for example, in U.S. Patent 1,882,279 issued October 11, 1932. Similarly British Patent 814,772 issued June 10, 1959, East German Patent 14,296 published January 6, 1958 and Jaag in Seifen, Ole, Fette, Wachse 88, No. 24, pp. 789—793 (November 1962) disclose enzyme-containing detergent compositions. Proteolytic enzymes aid the cleaning process by degrading or otherwise altering proteinaceous stains and rendering them more easily removable by the deterative action of a detergent compound. In addition, their degradative action serves to digest or break down proteinaceous materials which serve as binding agents for nondigestible soils.

Various attempts have been made in the art to formulate enzyme-containing detergent compositions incorporating an enzyme material having suitable compatibility with synthetic detergents and appreciable proteolytic activity. These attempts have involved the formulation of detergent compositions having appreciable amounts of inorganic phosphorus-containing builders, e.g., sodium tripolyphosphate or pyro-phosphates. While these enzyme-containing detergent compositions provide high levels of cleaning, including efficient stain-removing properties, the phosphorus content of such compositions may have adverse environmental effects, such as accelerated eutrophication of lakes.

Eutrophication is a natural process which is vital to sustaining the life of any lake or stream by enabling plant organisms to grow in the water and thus provide food for fish.

One of the main concerns today is "excessive" or "accelerated" eutrophication. Too much plant life in lakes and streams consumes the oxygen needed by fish and thus destroys the proper ecological balance in these bodies of water. This excessive eutrophication is caused by too many nutrients going into lakes and streams. The phosphates, which are found in the most generally used solid detergent compositions, are one such nutrient. However, phosphates by themselves do not cause excessive eutrophication. Other nutrients, such as carbon and nitrogen must also be present. It is the combination of nutrients which stimulates the growth of plant life in lakes and streams.

It is an object of this invention to provide biodegradable detergent compositions that are free from phosphate builders, and are effective in water solutions over a wide range of concentrations and pH's inasmuch as the conditions under which household laundry is done vary quite widely; also to attain an enhanced building action particularly in heavy-duty laundry detergent compositions.

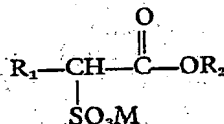
This invention is based on the discovery that a superior level of cleaning can be attained with detergent compositions comprising a certain critical surface-active agent

and citrate builders. A preferred embodiment of the invention comprises incorporating enzymes into the above surface-active agent and citrate compositions. The invention thus involves the preparation of laundry detergent compositions comprising a combination of essential components.

According to the invention, a detergent composition comprises:

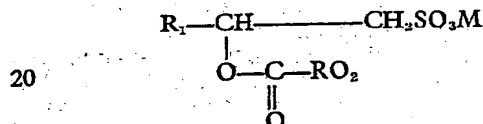
- 10 A. from 10% to 85% by weight of synthetic organic detergent or mixture of detergents selected from the following:

(i) compounds of the formula:



- 15 where R_1 is alkyl or alkenyl having from 10 to 20 carbon atoms, R_2 is alkyl having from 1 to 10 carbon atoms and M is a salt-forming radical,

(ii) compounds of the formula



where R_1 is alkyl having from 9 to 23 carbon atoms, R_2 is alkyl having from 1 to 8 carbon atoms and M is a salt-forming radical,

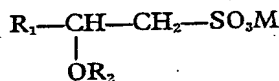
(iii) compounds of the formula:



where R is alkyl or alkenyl having from 10 to 20 carbon atoms, x is within the range from 1 to 30 and M is a salt-forming radical,

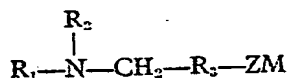
- 30 (iv) olefin sulphonates having from 12 to 24 carbon atoms,

(v) compounds of the formula



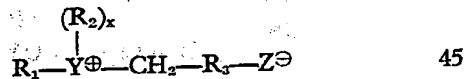
- 35 where R_1 is alkyl having from 8 to 20 carbon atoms, R_2 is alkyl having from 1 to 3 carbon atoms and M is a salt-forming radical,

(vi) compounds of the formula

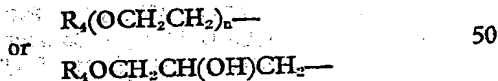


where R_1 is alkyl having from 8 to 18 carbon atoms, R_2 is alkyl having from 1 to 3 carbon atoms or is hydrogen, R_3 is alkylene having from 1 to 4 carbon atoms, Z is carboxy, sulphonate or sulphate and M is a salt-forming radical, 40

(vii) compounds of the formula

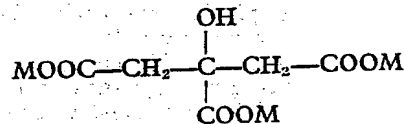


where R_1 is alkyl, alkenyl or hydroxyalkyl containing from 8 to 18 carbon atoms or a group



where R_4 is alkyl, alkenyl or hydroxyalkyl, n is 1-10 and R_4 has a total of 8-18 carbon atoms, Y is nitrogen, phosphorus or sulphur, R_2 is alkyl or monohydroxyalkyl having from 1 to 3 carbon atoms, x is 1 when Y is sulphur and 2 when Y is nitrogen or phosphorus, R_3 is alkylene or hydroxy alkylene having from 1 to 4 carbon atoms and Z is carboxylate, sulphonate, sulphate, phosphonate or phosphate; and 60

- B. from 10% to 75% by weight of a citrate having the formula



where M is hydrogen or a salt-forming radical; said laundry composition having a pH of from 6 to 10 in aqueous solution at a concentration of 0.12% by weight. 65

A preferred embodiment of the invention is a composition comprising Components A and B, described hereinabove, and from 0.001% to 5% of a proteolytic enzyme characterized by proteolytic activity in aqueous solution at temperatures of up to 130°F. in the pH selected in the range from 6 to 10. 70

The organic detergents which may be used in the preparation of detergent formulations effective in household laundering include certain anionic, zwitterionic and ampholytic detergents and mixtures thereof. The detergent compounds utilizable in the formulation of detergent compounds in accordance with the present invention, including those which have the preferred enzymes, are compounds which possess certain desirable properties. These properties include superior detergency and dispersancy and relative resistance to precipitation or insoluble complex formation 80 85

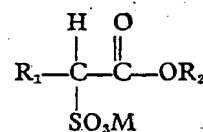
under the conditions of pH and water hardness contemplated herein including washing conditions or compositions which correspond to pH's in the range of 6 to 10. The terms detergency and dispersancy where employed herein refer, respectively, to the capacity to remove particulate and lipid soils from a substrate and the capacity to maintain in suspension in a washing solution, the particulate and lipid soils removed from a substrate by deterative action. Detergent and dispersant compounds utilizable herein must, in addition, perform satisfactorily in washing solutions containing hard water mineral ions normally present in tapwater, e.g. without forming a precipitate or non-detergent insoluble complex. Where a detergent and dispersant material forms such a precipitate or insoluble complex with hard water ions, the material is rendered into a relatively useless form and thereby does not function in its intended manner. A suitable detergent and dispersant material for use herein is one that does not form the hereinbefore described undesirable materials in tap water of normal hardness.

It has been found quite unexpectedly that the excellent levels of cleaning and whitening which heretofore have been attainable only from detergent compositions containing phosphate builders can be attained by employing a detergent composition which comprises a synthetic organic detergent having the hereinbefore described properties in combination with a citrate compound. The preferred embodiment, which employs enzymes, provides superior cleaning and whitening.

The synthetic organic detergent compounds utilizable herein and having the hereinbefore described properties include certain anionic, ampholytic and zwitterionic materials. These materials include water-soluble salts of certain materials such as sulfonated fatty acid esters of β - acyloxyalkane - 1 - sulfonic acid; β - alkyloxy alkane sulfonates; alkyl polyoxyethylene sulfates, water-soluble olefin sulfonates; and certain ampholytic and zwitterionic detergents. Of the organic detergents investigated, only detergents more specifically described hereinafter have been found to provide, in the compositions of the present invention, the levels of cleaning which equal or surpass those normally attained in the course of washing with a conventional detergent composition. Only the hereinafter described highly efficient detergent compounds have been found to permit the attainment of levels of cleaning comparable to those obtainable heretofore with phosphate builder compositions. It will be appreciated that mixtures of these detergent materials can be employed to advantage.

Anionic organic detergents utilizable herein include alkali metal, ammonium and substituted-ammonium salts of esters of an α -

sulfonated fatty acid. These detergent compounds have the following structure:



wherein R_1 is alkyl or alkenyl having from 10 to 20 carbon atoms (forming with the two carbon atoms a fatty acid group); R_2 is alkyl having from 1 to 10 carbon atoms; and M is a salt-forming radical.

The salt-forming radical M in the hereinbefore described structural formula is a water-solubilizing cation and can be, for example, an alkali metal cation (e.g. sodium, potassium, lithium), ammonium or substituted-ammonium cation. Specific examples of substituted ammonium cations include: methyl-, dimethyl-, and trimethyl- ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperidinium cations and those derived from alkylamines such as ethylamine, diethylamine, triethylamine and mixtures thereof.

Specific examples of this class of compounds include the sodium and potassium salts of esters where R_2 is selected from methyl, ethyl, propyl, butyl, hexyl and octyl groups and the fatty acid group (R_1 plus the two carbon atoms in the structure above) is selected from lauric, myristic, palmitic, stearic, palmitoleic, oleic, linoleic acids and mixtures thereof. A preferred ester material herein is the sodium salt of the methyl ester of α -sulfonated tallow fatty acid, the term tallow indicating a carbon chain distribution approximately as follows:

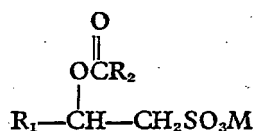
C_{14} —2.5%, C_{16} —28%, C_{18} —23%, palmitoleic—2%, oleic—41.5%, and linoleic—3% (the first three fatty acids listed are saturated).

Other examples of suitable salts of α -sulfonated fatty esters utilizable herein include the ammonium and tetramethyl-ammonium salts of the hexyl, octyl, ethyl, and butyl esters of α -sulfonated tridecanoic acid; the potassium and sodium salts of the ethyl, butyl, hexyl, octyl, and decyl esters of α -sulfonated pentadecanoic acid; and the sodium and potassium salts of butyl, hexyl, octyl, and decyl esters of α -sulfonated heptadecanoic acid; and the lithium and ammonium salts of butyl, hexyl, octyl, and decyl esters of α -sulfonated nonadecanoic acid.

The salts of α -sulfonated fatty acid esters of the present invention are known compounds and are described in U.S. Patent 3,223,645, issued December 14, 1965 to Kalberg.

Another class of suitable anionic organic

detergents includes salts of 2 - acyloxy - alkane - 1 - sulfonic acids. These salts have the formula



- 5 where R_1 is alkyl having from 9 to 23 carbon atoms (forming with the two carbon atoms an alkane group); R_2 is alkyl having from 1 to 8 carbon atoms; and M is a salt-forming radical as hereinbefore described.
- 10 Specific examples of β - acyloxy - alkane - 1 - sulfonates, or alternatively 2 - acyloxy - alkane - 1 - sulfonates, utilizable herein to provide excellent cleaning levels under household washing conditions include: the sodium salt of 2 - acetoxy - tridecane - 1 - sulfonic acid; the potassium salt of 2 - propionyloxy - tetradecane - 1 - sulfonic acid; the lithium salt of 2 - butanoyloxy - tetradecane - 1 - sulfonic acid; the sodium salt of 2 - pentanoyloxy - pentadecane - 1 - sulfonic acid; the ammonium salt of 2 - hexanoyloxy - hexadecane - 1 - sulfonic acid; the sodium salt of 2 - acetoxy - hexadecane - 1 - sulfonic acid; the dimethylammonium salt of 2 - heptanoyloxy - tridecane - 1 - sulfonic acid; the potassium salt of 2 - octanoyloxy - tetradecane - 1 - sulfonic acid; the dimethylpiperidinium salt of 2 - nonanoyloxy - tetradecane - 1 - sulfonic acid; the sodium salt of 2 - acetoxy - hepta - decane - 1 - sulfonic acid; the lithium salt of 2 - acetoxy - octadecane - 1 - sulfonic acid; the dimethylamine salt of 2 - acetoxyoctadecane - 1 - sulfonic acid; the potassium salt of 2 - acetoxy - nonadecane - 1 - sulfonic acid; the sodium salt of 2 - acetoxy - uncosane - 1 - sulfonic acid; the sodium salt of 2 - propionyloxy - docosane - 1 - sulfonic acid; and isomers thereof.

- 40 Preferred β - acyloxy - alkane - 1 - sulfonate salts herein are the alkali metal salts of β - acetoxy - alkane - 1 - sulfonic acids corresponding to the above formula wherein R_1 is an alkyl having from 14 to 18 carbon atoms. These salts are preferred from the standpoints of their excellent cleaning properties and ready availability.

- 45 Typical examples of the above described β -acetoxy alkanesulfonates are described in the literature: Belgian Patent 650,323 issued July 9, 1963, discloses the preparation of certain 2-acyloxy alkanesulfonic acids. Similarly, U.S. Patents 2,094,451 issued September 28, 1937, to Guenther et al. and 2,086,215 issued July 6, 1937 to DeGroote disclose certain salts of β -acetoxy alkanesulfonic acids.

55 Other synthetic anionic detergents useful herein are alkyl ether sulfates. These materials have the formula



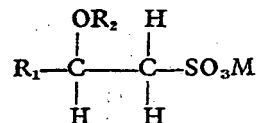
wherein R is alkyl or alkenyl having from 10 to 20 carbon atoms, x is from 1 to 30, and M is a salt-forming cation as defined hereinbefore.

60 The alkyl ether sulfates of the present invention are condensation products of ethylene oxide and monohydric alcohols having from 10 to 20 carbon atoms. Preferably, R has 14 to 18 carbon atoms. The alcohols can be derived from fats, e.g. coconut oil or tallow, or can be synthetic. Lauryl alcohol and straight chain alcohols derived from tallow are preferred herein. Such alcohols are reacted with 1 to 30, and especially 3 to 6, molar proportions of ethylene oxide and the resulting mixture of molecular species, having, for example, an average of 3 to 6 moles of ethylene oxide per mole of alcohol, is sulfated and neutralized.

Specific examples of alkyl ether sulfates of the present invention are: sodium coconut alkyl ethylene glycol ether sulfate; lithium tallow alkyl triethylene glycol ether sulfate; sodium tallow alkyl hexaoxyethylene sulfate; and ammonium tetradecyl octaoxyethylene sulfate.

Preferred herein for reasons of excellent cleaning properties and ready availability are the alkali metal coconut- and tallow-alkyl oxyethylene ether sulfates having an average of 1 to 10 oxyethylene moieties. The alkyl ether sulfates of the present invention are known compounds and are described in U.S. Patent 3,332,876 (Walker).

A preferred class of anionic organic detergents are the β -alkoxy alkane sulfonates. These compounds have the following formula:



where R_1 is a straight chain alkyl group having from 8 to 20 carbon atoms, R_2 is a lower alkyl group having from 1 to 3 carbon atoms, and M is a salt-forming radical as hereinbefore described.

Specific examples of β -alkoxy alkane sulfonates or alternatively 2 - alkoxyloxy - alkane - 1 - sulfonates, utilizable herein to provide superior cleaning and whitening levels under household washing conditions include:

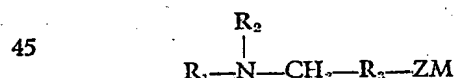
potassium β -methoxydecane sulfonate,
sodium β - methoxy - tridecane sulfonate,
potassium β - ethoxytetradecyl sulfonate,
sodium β - isopropoxyhexadecyl sulfonate,
lithium β - butoxytetradecyl sulfonate,
sodium β - methoxyoctadecyl sulfonate, and
ammonium β - n - propoxydodecyl sulfonate.

Other suitable anionic detergents utilizable herein are olefin sulfonates having from 12 to 24 carbon atoms. The term "olefin sulfonates" is used herein to mean compounds which are produced by the sulfonation of α -olefin by means of uncomplexed sulfur trioxide, followed by neutralization of the acid reaction mixture under conditions such that any sulfones which have been formed in the reaction are hydrolyzed to give the corresponding hydroxy - alkane - sulfonates. The sulfur trioxide may be liquid or gaseous, and is usually, but not necessarily, diluted by inert diluents, for example by liquid SO_2 , chlorinated hydrocarbon, etc., when used in the liquid form, or by air, nitrogen, gaseous SO_2 , etc., when used in the gaseous form.

The α -olefins from which the olefin sulfonates are derived are mono-olefins having 12 to 24 carbon atoms, preferably 14 to 16 carbon atoms. Preferably, they are straight chain olefins. Examples of suitable 1-olefins include 1-dodecene; 1-tetradecene; 1-hexadecene; 1-octadecene; 1-eicosene and 1-tetracosene.

In addition to the true alkene sulfonates and a proportion of hydroxy - alkanesulfonates, the olefin sulfonates can contain minor amounts of other materials, such as alkene disulfonates depending upon the reaction conditions, proportions of reactants, the nature of the starting olefins and impurities in the olefin stock and side reactions during the sulfonation process.

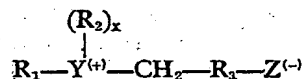
Ampholytic synthetic detergents utilizable herein can be broadly described as derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight chain or branched and wherein one of the aliphatic substituents contains from 8 to 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, or sulfate. These detergents have the formula



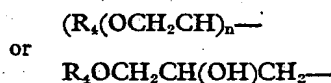
wherein R_1 is alkyl having from 8 to 18 carbon atoms, R_2 is alkyl having from 1 to 3 carbon atoms or is hydrogen, R_3 is alkylene having from 1 to 4 carbon atoms, Z is carboxy, sulfonate, or sulfate, and M is a salt-forming cation. Examples of compounds falling within this definition are sodium 3 - dodecylaminopropionate; sodium 3 - dodecylaminopropane sulfonate; N - alkyltaurines such as the ones prepared by reacting dodecylamine with sodium isethionate according to the teaching of U.S. Patent 3,658,072; sodium salts of N-higher alkyl aspartic acids such as those produced according to the teaching of U.S. Patent 2,438,091; and the products sold

under the trade name "Miranol" and described in U.S. Patent 2,528,378.

Zwitterionic synthetic detergents of the present invention can be broadly described as derivatives of aliphatic quaternary ammonium, and sulfonium compounds, in which the aliphatic radicals can be straight chain or branched, and wherein one of the aliphatic substituents contains from 8 to 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate or sulfate. A general formulae for these compounds is:



wherein R_1 contains an alkyl, alkenyl, or hydroxyalkyl radical having from 8 to 18 carbon atoms or a group



where R_4 is alkyl, alkenyl or hydroxyalkyl, n is 1-10 and R_4 has a total of 8-18 carbon atoms; Y is nitrogen phosphorus or sulfur; R_2 is an alkyl or monohydroxy alkyl group containing 1 to 3 carbon atoms; x is 1 when Y is a sulfur atom and 2 when Y is a nitrogen or phosphorus atom, R_3 is an alkylene or hydroxy alkylene of from 1 to 4 carbon atoms and Z is carboxylate, sulfonate, sulfate, phosphonate or phosphate.

Examples of these detergents include: 4 - [N,N - di(2 - hydroxyethyl) - N - octadecylammonio] - butane - 1 - carboxylate; 5 - [S - 3 - hydroxypropyl - S - hexadecylsulfonio] - 3 - hydroxypentane - 1 - sulfate; 3 - [P,P - diethyl - P - 3,6,9 - trioxatetracosanephosphonio] - 2 - hydroxypropane - 1 - phosphate; 3 - [N,N - dipropyl - N - 3 - dodecoxy - 2 - hydroxypropylammonio] - propane - 1 - phosphonate; 3 - (N,N - dimethyl - N - hexadecylammonia)propane - 1 - sulfonate, 3 - (N,N - dimethyl - N - hexadecylammonia) - 2 - hydroxypropane - 1 - sulfonate, 4 - [N,N - di(2 - hydroxyethyl) - N - (2 - hydroxydodecyl)ammonio] - butane - 1 - carboxylate, 3 - [S - ethyl - S - (3 - dodecoxy - 2 - hydroxypropyl)sulfonio] - propane - 1 - phosphate, 3 - [P,P - dimethyl - P - dodecylphosphonio]propane - 1 - phosphonate, and 3 - [N,N - di(3 - hydroxypropyl) - N - hexadecylammonio] - 2 - hydroxypentane - 1 - sulfonate. Preferred examples of compounds falling within this definition are: 3 - (N,N - dimethyl - N - hexadecylammonio)propane - 1 - sulfonate and 3 - (N,N - dimethyl - N - tri-dodecylammonio) - 2 - hydroxypropane - 1 - sulfonate. These compounds are especially

preferred for their excellent cool water detergent characteristics.

5 The alkyl groups contained in said detergent surfactants can be straight or branched, preferably straight, and saturated or unsaturated as desired.

10 The detergent compounds of the present invention are employed in varying amounts in the enzyme-containing detergent compositions of the present invention. As there will be considerable variation in the strengths of washing solutions employed by different users, i.e., some users may tend to use more or less than others, the requisite amount of detergent compound in the detergent formulation is an amount sufficient to provide superior cleaning and whitening levels under diverse conditions of soiling and usage. The enzyme-containing detergent compositions of the present invention can contain from 10 to 85% by weight of the synthetic organic detergent depending upon the detergent employed. A preferred amount of detergent is from 15 to 50%.

25 The enzyme suitable for use in the detergent compositions of this invention are solid, catalytically active protein materials which degrade or alter one or more types of soil or stains encountered in laundering situations so as to remove the soil or stain from the fabric or object being laundered or make the soil or stain easier to remove in a subsequent laundering step. Both degradation and alteration improve soil removability. As used herein, enzyme activity refers to the ability of an enzyme to perform the desired function of soil attack and enzyme stability refers to the ability of an enzyme to remain in an active state.

40 The enzymatic components utilizable herein are those which exhibit their degradative and/or altering effects on proteinaceous soils and stains under the washing conditions contemplated herein, i.e., those which exhibit proteolytic activity in aqueous solutions at pH's ranging from 6 to 10 and at temperatures of 50°F. to 130°F.

50 Whilst not wishing to be bound by any particular theory or mechanism, it is believed that the proteolytic enzymes of the present invention catalyze the hydrolysis of the peptide linkage of proteins, polypeptides and related compounds to free amino and carboxyl groups and thus break down the protein structure in soil. Suitable proteolytic enzymes for use herein include those materials which are termed in the art neutral proteases. These materials exhibit the peak of their proteolytic activity in the substantially neutral range of pH contemplated herein. Also utilizable herein are proteolytic enzymes known in the art as alkaline proteases. These materials exhibit their peak enzymatic effects in the more alkaline solutions of this invention. Therefore, the pH of the solution formed

by the active synthetic detergent and the builder mixtures of this invention, once determined, will dictate which of the many proteases disclosed herein should be used in each particular case.

70 The amount of proteolytic enzyme employed herein to provide the preferred detergent compositions of the present invention is not critical, and is an amount of proteolytic enzyme capable of effecting the degradation of the proteinaceous matter normally encountered in a home laundering situation under the washing conditions contemplated herein, e.g., at temperatures of 50°F. to 130°F. and at pH's of from 6 to 10. Normally, the proteolytic enzyme is employed in an amount of 0.001 to 5% by weight of the enzyme-containing detergent composition on a pure enzyme basis. Best results in terms of overall cleaning efficacy and stain-removing properties are attained when the proteolytic enzyme is employed in an amount of from 0.01 to 1%.

90 The above-described proteases can be utilized in a pure form in the preparation of enzyme-containing detergent compositions. Generally, however, powdered commercial enzyme compositions containing these enzymes are utilized herein because these compositions are easier to handle and retain their activity for a longer period of time. These commercial compositions are therefore preferred for use herein, and can contain from 2% to 80% of active neutral, alkaline and mixtures of neutral and alkaline proteases in combination with inert powdered materials which comprise the remaining 20% to 98%. These powdered materials can comprise: inorganic alkali metal salts such as sodium sulfate; sodium chloride, potassium silicate, and sodium phosphate; inorganic alkaline earth metal salts such as calcium sulfate, magnesium sulfate, magnesium phosphate and the like; organic components such as non-enzymatic proteins, carbohydrates, organic clays, starches, lipids, color bodies, and the like. Active enzyme content of a commercial product is a result of manufacturing methods employed and is not critical herein so long as the finished compositions have desired enzymatic soil and stain-removing properties.

120 The enzymes per se have molecular diameters of from about 30 Angstroms to several thousand Angstroms. However, the particle diameters of the enzyme powder as utilized herein are normally much larger due to agglomeration of individual enzyme molecules or addition of inert powdered materials or vehicles such as starch, organic clays, sodium or calcium sulfate or sodium chloride, during enzyme manufacture. Organic clays are clays (e.g. montmorillonite, bentonite) which have been modified by treatment with organic cationic compounds to give clay-

organo-philic properties. Enzymes are frequently grown in solution. Such vehicles are added after filtration of such solution to precipitate the enzyme in fine form which is then dried; calcium salts also stabilize some enzymes. The enzyme powders of this invention, including those employed in the Examples, are typically fine enough to pass through a Tyler Standard 20 mesh screen (0.85 mm.) although larger agglomerates are often found. Some particles of commercially available enzyme powders are fine enough to pass through a Tyler Standard 100 mesh screen. Generally a major amount of particles will remain on a 150 mesh screen. Thus, the powdered enzymes utilized herein usually range in size from about 1 mm. to 1 micron, most generally from 1 mm. to 0.01 mm. The enzyme powders of the examples have particle size distributions in these ranges.

The activity of the proteases of the present invention can be readily expressed in terms of activity units, e.g., casein assay activity units. In accordance with the casein assay method of determining proteolytic activity, a solution of the protease to be evaluated is allowed to digest, by hydrolysis, a solution of casein substrate at an appropriate pH and temperature. The reaction is stopped by the addition of trichloroacetic acid, the solution is filtered and the color of the filtrate containing the digested casein is developed employing Folin-Ciocalteu phenol reagent. The degree of enzymatic activity is determined by comparing the spectrophotometric response with that of solutions of varying concentrations of reagent grade tyrosine and determining the amount of tyrosine produced. The casein assay method of determining proteolytic activity is well known and a more detailed discussion is found in B. Hagihara et al, J. Biochem. (Tokyo), 45, 185 (1958) and M. Kunitz, J. Gen. Physiol., 291 (1947).

The activities of the proteases of the present invention vary depending largely upon the concentration of proteases in the enzymatic composition, upon calcium ion concentration, upon substrate concentration, and upon pH. Pure samples of proteases of the present invention are highly active. For example, a *Bacillus subtilis*-derived Carlsberg subtilisin employed herein is characterized by a protease activity unit number on a pure basis of about 7,500,00 units/gram. Commercially available compositions wherein the protease is present in varying amounts with inert filler material or vehicle vary in activity from 100,000 to 1,500,000 units/gram. Similarly, an x-ray mutated *Bacillus subtilis*-derived subtilisin suitable herein is characterized by an activity of about 7,500,000 units/gram, on a pure basis, while the commercial preparations vary in activity from 100,000 to 1,500,000 units/gram.

As described hereinbefore, the amount of protease employed herein in the enzyme-containing detergent compositions of the present invention is from 0.001 to 5% of the composition, on a pure enzyme basis. This amount corresponds to the incorporation into the detergent composition of about 75 to about 375,000 protease activity units/gram of detergent composition. When a commercially available enzyme preparation is employed as described hereinbefore, from 0.03% to 10% of the preparation is utilized.

Preferably, from 0.1% to 5% is employed and provides excellent soil- and stain-degrading properties. It will of course be appreciated that the amount of enzymatic composition required in the formulation of detergent compositions having a desired level of proteolytic activity varies with the activity level of the enzyme-containing composition employed. A mixture of proteolytic enzyme and inert carrier wherein the protease is present in a minor amount, e.g., about 2%, will be employed in a larger amount than a mixture which contains a greater amount, e.g., about 80%, of proteolytic enzyme. The precise amounts of such materials employed in the formulation of enzyme-containing detergent compositions can be readily determined by methods known in the art so long as the requisite amount of protease hereinbefore specified is employed.

Specific examples of proteases suitable for use in this invention are: trypsin, collagenase, keratinase, elastase, subtilisin, BPN and BPN'.

Preferred proteolytic enzymes herein are those derived from the bacterial organism *Bacillus subtilis* and termed subtilisins. These materials are preferred from the standpoints of excellent soil- and stain-removing properties, desirable temperature stability and activity, and ready availability. Also preferred are those proteases derived from the *Streptomyces* class of microorganisms.

A preferred subtilisin of the present invention is the *Bacillus subtilis*-derived Carlsberg strain. The Carlsberg strain employed in accordance with the present invention is a known subtilisin strain, the amino acid sequence of which is described in Smith et al., "The Complete Amino Acid Sequence of Two Types of Subtilisin, BPN' and Carlsberg", J. of Biol. Chem., Volume 241, December 25, 1966 at page 5974. This subtilisin strain is characterized by a tyrosine to tryptophan ratio of about 13 to 1. The above reference including its description, of the amino acid sequence of the Carlsberg subtilisin is hereby incorporated by reference.

An x-ray mutated *Bacillus subtilis*-derived subtilisin constitutes another preferred subtilisin of the present invention. This mutation can be effected in accordance with U.S. Patent 3,031,380 issued April 24, 1962 to

Minagawa *et al.* by irradiation of a *Bacillus subtilis* organism with x-rays. Subsequent treatment in a conventional manner can be employed to result in the preparation of an enzymatic composition. U.S. 3,031,380 describes a process whereby an enzymatic composition is produced by subjecting *Bacillus subtilis* to x-rays of an intensity corresponding substantially to 24—50 roentgens for an interval of at least half an hour, selecting from the colony thus subjected to x-rays a strain identified by cells having hairless, rough, jagged, spotted and dull white characteristics, separating said strain and placing the separated strain in a culture selected from the group consisting of wheat bran and corn meal, maintaining the culture for a period of at least 40 hours while aerating the culture substantially continuously, and drying the culture.

Specific examples of commercial enzyme products and the manufacturer thereof include: Alcalase, Novo Industri, Copenhagen, Denmark; Maxatase, Koninklijke Nederlandsche Gist-En Spiritusfabriek N.V., Delft, Netherlands; Protease B-4000 and Protease AP, Schweizerische Ferment A.G., Basel, Switzerland; CRD-Protease, Monsanto Company, St. Louis, Missouri; Viokase, VioBin Corporation, Monticello, Illinois; Pronase-E, Pronase-AS and Pronase-AF all of which are manufactured by Kaken Chemical Company, Japan, Rapidase P-2000, Rapidase, Seclin, France; Takamine, HT Proteolytic enzyme 200, Enzyme L-W (derived from fungi rather than bacteria), Miles Chemical Company, Elkhart, Indiana; Rhozyme P-11 concentrate, Rhozyme PF, Rhozyme J-25, Rohm & Haas, Philadelphia, Pennsylvania; Rhozyme PF and J-25 have salt and corn starch vehicles and are proteases having diastase activity; Amprozime 200, Jacques Wolf & Company, a subsidiary of Nopco Chemical Company, Newark, New Jersey; Takeda Fungal Alkaline Protease, Takeda Chemical Industries, Ltd., Osaka, Japan; Wallerstein 201-HA, Wallerstein Company, Staten Island, New York; Protein AS-20, Dawai Kasei K.K., Osaka, Japan; and Protease TP (derived from thermophilic *Streptomyces* species strain 1689), Central Research Institute of Kikkoman Shoya, Noda Chiba, Japan.

Protease TP, its properties and characteristics, as well as methods for its preparation are described in Agr. Biol. Chem., 28, No. 12, pp. 884—895, December, 1964: Studies on the Proteolytic Enzymes of Thermophilic *Streptomyces*, Part I. Purification and Some Properties; Agr. Biol. Chem., 30, No. 1, pp. 35—41, January, 1966: Studies on the Proteolytic Enzymes of Thermophilic *Streptomyces*, Part II. Identification of the Organism and Some Conditions of Protease Formation; and Applied Microbiology, 17, No. 3, March

1969. The authors are Mizusawa *et al.* This enzyme is preferred when the excellent washing solution is in the pH range of 9—10.

CRD Protease (also known as Monsanto DA-10) is useful powdered enzyme product. CRD-Protease is reported to be obtained by mutation of a *Bacillus subtilis* organism. Its proteolytic enzyme is about 80% neutral protease and 20% alkaline protease. The neutral protease has a molecular weight of about 44,000 and contains from 1 to 2 atoms of zinc per molecule. It also exhibits amylolytic activity. Its particle size ranges predominantly from 0.03 mm. to 0.1 mm. and it can be prepared to range in active enzyme content from 20% to 75%. This enzyme can be utilized in the compositions of this invention in the pH range of 6—8 giving excellent results.

Pronase-P, Pronase-E, Pronase-AS and Pronase-AF are powdered enzyme products which can also be used to advantage in this invention. These enzymes are produced from the culture broth of *Streptomyces griseus* used for streptomycin manufacture. They are isolated by the successive resin column treatment. A major component of the Pronase is a neutral Protease named as *Streptomyces griseus* protease. This enzyme product is useful herein and provides excellent soil- and stain-removing properties.

Another enzyme product preferred for use in the detergent compositions of this invention, having a pH in the range of 8—9, as illustrated in the Examples below, is a proteolytic enzyme a serine protease, manufactured by Novo Industri A/S, Copenhagen, Denmark, and sold under the trade name of Alcalase. Alcalase is described, in a trade bulletin bearing that name which was published by Novo Industri A/S, as a proteolytic enzyme preparation manufactured by submerged fermentation of a special strain of *Bacillus subtilis*. The primary enzyme component of Alcalase is subtilisin. Alcalase is a fine grayish, free-flowing powder having a crystalline active enzyme content of about 6% and a particle size ranging from 1.2 mm. to 0.01 mm. and small, about 75% passing through a 150 mesh Tyler screen. The remainder of the powder is comprised primarily of sodium sulfate, calcium sulfate and various inert organic vehicle materials. Alcalase can be advantageously used with the synthetic detergent compositions of this invention.

The citrate compounds which are essential components of the compositions of the present invention include citric acid and salts thereof, collectively termed citrates and are characterized by the capacity to sequester calcium ions from aqueous solution.

The citrates useful herein are those having sufficient calcium sequestration properties to reduce the calcium ion concentration of an

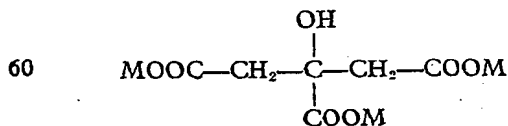
aqueous solution containing 1.2×10^{-3} M of calcium ion to a concentration of 1.7×10^{-4} M or less when employed in an amount of up to 0.1% of the solution.

5 The sequestration capacity of the citrate compounds useful herein can be determined conveniently by detecting the amount of calcium ion remaining in aqueous solution following the addition of a citrate sequestrant
10 herein. The level of calcium ion in an aqueous solution can be determined by a calcium electrode which operates by developing an electrical potential across a thin layer of water-immiscible liquid ion exchanger. This
15 liquid is held mechanically rigid by a thin porous inert membrane disc. The liquid ion exchanger, a calcium salt of an organophosphoric acid, exhibits a very high specificity for calcium ions. An internal filling solution
20 of calcium chloride contacts the inside surface of the membrane disc. The calcium ion in this solution provides a stable potential between the inside of the membrane and the filling solution, while the chloride ion provides a stable potential between a silver-silver
25 chloride internal reference electrode and the filling solution. Thus, changes in potential are due only to changes in sample calcium ion activity.

30 The electrode responds only to the ionized or unbound calcium in the sample. The electrode does not respond to that portion of the calcium which is bound to a sample of polycarboxylate of the invention. The calcium
35 concentration can be determined by detection of the electrode potential and comparison with a calibration curve of calcium ion concentration and electrode potential.

40 The calcium sequestering capacity of the citrates of the invention is measured by adding increments of a solution of the citrate, preferably as an acid or potassium salt form, to a 1.2×10^{-3} M calcium chloride solution
45 over a period of 1 hour at a temperature of 25°C . The electrical potential is measured with each incremental addition, the additions being continued until no further sequestration decreases in calcium ion concentration is
50 detected or until the concentration of added citrate is 0.1% of the solution. Citrate sequestrants useful herein reduce calcium ion concentration, under the conditions of this test, to 1.7×10^{-4} M or less when employed at a
55 concentration of up to 0.1%. Preferred citrates herein reduce the concentration to 1.7×10^{-4} M or less by the addition of from 0.03 to 0.06%.

The citrates used herein have the following formula:



where M is hydrogen or a salt forming radical or water solubilizing cation which does not interfere with the cleaning process. Preferred cations are alkali metals such as sodium, potassium, and lithium; ammonium; substituted ammonium such as mono-, di-, and tri-methylol ammonium, mono-, di-, and tri-ethanolammonium cations.

A suitable calcium electrode for measuring calcium ion concentration and sequestration capacity of the citrates of the invention is available as model 92-20 from Orion Research Incorporated, (11 Blackstone Street, Cambridge, Massachusetts).

Any of the citrate compounds described hereinbefore and including the acids and salts can be employed in the formulation of compositions of the invention. Citrate compounds wherein each acidic hydrogen atom is replaced by a water-solubilizing cation tend to render the compositions of the invention alkaline. Conversely, those which contain no water-solubilizing cations tend to render the compositions acidic.

The detergent compositions of this invention can be prepared in any suitable physical form such as granules (e.g., either spray-dried or mechanically mixed), flakes, tablets, pastes, or liquids.

The detergent compositions of this invention can be formulated by methods known to those skilled in the art. For example, a mixture of organic detergent and citrate compound utilizable herein can be employed in the form of spray-dried or agglomerated granules or in the form of a mechanical mixture of granular organic detergent and citrate compounds. Detergent granules can range in size from about 100% through a Tyler Standard 6-mesh screen (3.33 mm.) to about 100% on a Tyler Standard 200-mesh screen (0.074 mm.). Segregation of granules in the detergent composition is minimized when the particle size of the granules ranges from about 100% through a Tyler Standard 12-mesh screen (1.4 mm.) to about 100%, on a Tyler Standard 100-mesh screen (0.15 mm.); this latter particle size range is preferred. The bulk density of the detergent granules, in order to reduce segregation, preferably ranges from 0.2 gms/cc. to 0.8 gms/cc.

A mixture of detergent and citrate compounds or granules thereof can be mechanically admixed with a proteolytic enzyme described hereinbefore to provide detergent compositions having the advantageous cleaning and soil- and stain-removing properties hereinbefore described.

It is normally preferred that the proteolytic enzyme hereinbefore described be incorporated into the detergent compositions of the present invention in a manner which minimizes segregation of the enzyme, preserves proteolytic activity, and enhances the soil-

and stain-removing properties of the detergent composition. For example, the enzyme can be mixed with water into a slurry and sprayed onto one or more granular components comprising the detergent compositions of this invention and which serve as granular carriers for the enzyme material. The resulting enzyme-containing granules can be employed as washing compositions *per se* or can be admixed with any remaining components of the compositions of the invention. Detergent compositions comprising enzyme-containing granules admixed with enzyme-free detergent granules are especially suitable.

A finished detergent formulation of this invention will often contain minor amounts of additional materials which make the product more effective or more attractive. The following are mentioned by way of example: soluble sodium carboxymethylcellulose can be added in minor amounts to inhibit soil redeposition; a tarnish inhibitor such as benzotriazole or ethylenethiourea can also be added in amounts up to about 2%; fluorescers, perfume and color, while not essential in the compositions of the invention, can be added in amounts up to about 1%. There might also be mentioned as suitable additives, water, other enzymes such as amylases, brightening agents and bleaching agents such as sodium perborate. The compositions may contain inorganic salts such as sodium sulphate and sodium chloride and other phosphate free builders such as sodium silicate and sodium carbonate.

The behaviour and mechanism by which the detergent, enzyme and citrate components of the preferred embodiment of the present invention operate to provide unexpectedly high levels of cleaning is not completely understood. Unequivocal criteria and principles do not exist which would permit one to predict which components in combination would possess the levels of cleaning exhibited by the compositions of the invention. The sodium salts of linear alkyl benzene sulfonate or tallow alkyl sulfate, for example, the excellent detergent materials believed to be more efficient cleaners than ethoxylated tallow alkyl sulfates. Compositions of the invention embodying an ethoxylated alkyl sulfate, sodium citrate and a proteolytic enzyme provide higher levels of cleaning than compositions containing the sodium salt of a linear alkyl benzene sulfonate or tallow alkyl sulfate in place of the ethoxylated alkyl sulfate. Moreover, compositions of the invention are more effective detergent compositions than conventional alkaline phosphate-built linear alkyl benzene sulfonate compositions.

The compositions of the present invention can be employed as pre-soak compositions to remove soil and strains prior to a separate laundering step or can be employed as a laundering product according to conven-

tional laundering methods. While the compositions of the invention are especially suitable for the laundering of textile materials, they can be employed as cleansing compositions in the washing of dishes, pots and pans, other hard surfaces such as walls and floors and the like.

The following Examples illustrate the novel compositions of the present invention. All amounts in the Examples are in parts by weight. The compositions of the following Examples provides washing solutions of pH 6 to 10 when dissolved in water.

EXAMPLE I

An excellent detergent composition for use in household laundering applications has the following ingredients:

	parts	
Sodium β - acetoxyhexadecane-sulfonate	20	85
Sodium citrate	60	
Sodium silicate ($\text{SiO}_2/\text{Na}_2\text{O}$ ratio of 1.6)	5	
Protease TP	0.8	
Sodium sulfate	15	90

EXAMPLE II

An excellent detergent composition giving outstanding cleaning results in substantially neutral laundering solutions has the following composition in the parts by weight indicated.

	parts	
Sodium salt of the methyl ester of α -sulfonated tallow fatty acid	35	100
Sodium citrate	25	
Sodium sulfate	30	
Sodium silicate ($\text{SiO}_2/\text{Na}_2\text{O}$ ratio of 1.6)	10	
Alkaline bacterial enzyme Protease TP	1	105

Substantially similar results can be obtained when the sodium salt of the methyl ester of α -sulfonated tallow fatty acid is replaced by the sodium, potassium and lithium salts of the methyl, ethyl, propyl, butyl, hexyl and octyl esters of α -sulfonated lauric, myristic, palmitic, stearic, palmitoleic, oleic and linoleic acids; the ammonium, dimethylammonium, tetramethylammonium, dimethyl piperidinium and diethanolamine salts of the methyl, ethyl, propyl, butyl, hexyl and octyl esters of α -sulfonated lauric, myristic, palmitic, stearic, palmitoleic, oleic and linoleic acids.

EXAMPLE III

Another excellent detergent composition for use in typical household laundering applications has the following ingredients:

		parts	
	Sodium β - acetoxy - hexadecane - 1 - sulfonate	40	
	Potassium citrate	40	
5	Sodium chloride	20	
	About 50% fungal neutral proteases in inerts (Pronase C)	0.6	

Substantially similar results can be obtained when the following electrolytes are employed in lieu of sodium chloride: sodium bromide; sodium nitrate; sodium sulfate.

- Substantially similar results can be obtained when the following β - acyloxy - alkane - 1 - sulfonates are employed in lieu of sodium β - acetoxy - hexadecane - 1 - sulfonate: the sodium salt of 2 - acetoxy - tridecane - 1 - sulfonic acid; the potassium salt of 2 - propionyloxy - tetradecane - 1 - sulfonic acid; the lithium salt of 2 - butanoyloxy - tetradecane - 1 - sulfonic acid; the sodium salt of 2 - pentanoyloxy - pentadecane - 1 - sulfonic acid; the ammonium salt of 2 - hexanoyloxy - hexadecane - 1 - sulfonic acid; the dimethylammonium salt of 2 - heptanoyloxy - tridecane - 1 - sulfonic acid; the potassium salt of 2 - octanoyl - oxytetradecane - 1 - sulfonic acid; the dimethylpiperdinium salt of 2 - nonanoyloxytetradecane - 1 - sulfonic acid; the sodium salt of 2 - acetoxy - heptadecane - 1 - sulfonic acid; the lithium salt of 2 - acetoxy - octadecane - 1 - sulfonic acid; the dimethylamine salt of 2 - acetoxy - octadecane - 1 - sulfonic acid; the potassium salt of 2 - acetoxy - nonadecane - 1 - sulfonic acid; the sodium salt of 2 - acetoxy - uncosane - 1 - sulfonic acid; the sodium salt of 2 - propionyloxy - docosane - 1 - sulfonic acid; and isomers thereof.

EXAMPLE IV

- Excellent cleaning results are obtained using a detergent composition prepared according to this invention and having the following ingredients.

		parts	
45	Sodium tallow trioxyethylene sulfate	35	
	Sodium citrate	30	
	Sodium silicate ($\text{SiO}_2/\text{Na}_2\text{O}$ ratio 1.6)	5	
50	Sodium sulfate	15	
	Sodium carbonate	15	
	Mixture of 6% Carlsberg subtilisin in inerts (Alcalase, Registered Trade Mark)	1	

- Substantially similar results can be obtained when the following enzymes are employed in lieu of Pronase E: Alcalase (Registered Trade Mark) and other enzymes, Novo Industri, Copenhagen, Denmark; Maxatase, Koninklijke Nederlandsche Gist-En Spiritusfabriek N.V., Delft, Netherlands; Protease B-4000 and Protease AP, Schweizerische Ferment A.G.,

Basel, Switzerland; CRD-Protease, Monsanto Company, St. Louis, Missouri; Viokase, VioBin Corporation, Monticello, Illinois; Pronase-P, Pronase-AS and Pronase-AF all of which are manufactured by Kaken Chemical Company, Japan, Rapidase P-2000, Rapidase Seclin, France; Takamine, HT proteolytic enzyme 200, Enzyme L-W (derived from fungi rather than bacteria), Miles Chemical Company, Elkhart, Indiana; Rhozyme P-11 concentrate, Rhozyme PF, Rhozyme J-25, Rohm & Haas, Philadelphia, Pennsylvania; Rhozyme PF and J-25 have salt and corn starch vehicles and are proteases having diastase activity; Amprozime 200, Jacques Wolf & Company, a subsidiary of Nopco Chemical Co., Newark, N.J.; Takeda Fungal Alkaline Protease, Takeda Chemical Industries, Ltd., Osaka, Japan; Wallerstein 201-HA, Wallerstein Co., Staten Island, New York, Protin AS-20, Dawai Kasei K.K., Osaka, Japan; and Protease TP (derived from thermophilic Streptomyces specie strain 1689), Central Research Institute of Kikkoman Shōyu, Noda Chiba, Japan.

EXAMPLE V

Superior cleaning effects are obtainable in neutral washing solutions with a detergent composition having the following ingredients:

		parts	
	Dimethylhexadecylammonio-propane sulfonate	20	
	Citric acid	40	95
	Sodium chloride	5	
	Sodium hydroxide	25	
	6% Carlsberg subtilisin in inerts (Alcalase Registered Trade Mark)	0.8	100

Comparable levels of cleaning are obtained when the following citrates are substituted for citric acid in whole or in part: disodium citrate, monopotassium citrate, and monoethanolammonium citrate.

EXAMPLE VI

A superior detergent composition effective in cleaning textile fabrics has the following composition:

		parts	
	Sodium β - methoxytetradecane sulfonate	35	
	Sodium citrate	30	
	Sodium sulfate	25	
	Sodium silicate ($\text{SiO}_2/\text{NaO}_2$ ratio of 1.6)	10	115
	Protease TP	0.8	

Substantially similar results can be obtained when the sodium β -methoxytetradecane sulfonate is replaced by the sodium, potassium, and lithium salts of β -methoxydecane, β -

ethoxytetradecyl sulfonate, β -isopropoxyhexadecyl sulfonate, β -t-butoxytetradecyl sulfonate, β -methoxyoctadecyl sulfonate, β -n-propoxydodecyl sulfonate, β -ethoxyoctadecyl sulfonate, and β -methoxyhexadecyl sulfonate.

Improved results are observed if 0.5 parts of 6% Carlsberg subtilisin in inerts (Alcalase) is added to the above composition.

EXAMPLE VII

The following composition provides excellent cleaning and contains the following ingredients:

	parts
Sodium tallow alkyl trioxyethylene sulphate	35
Sodium citrate	40
Sodium sulfate	25

The cleaning provided equals the non-enzyme linear alkyl benzene sulfonate-alkaline phosphate built products.

EXAMPLE VIII

The following composition provides excellent cleaning and contains the following ingredients:

	parts
Sodium salt of sulfonated - 1 - hexadecane	40
Sodium citrate	35
Sodium sulfate	10
Sodium bicarbonate	15
Mixture of 6% Carlsberg subtilisin in inerts (Alcalase)	0.6

Wash-wear tests using standardized detergent compositions described below were performed to illustrate the relative effectiveness of representative compositions of the present invention. A sodium tripolyphosphate-built anionic active-containing formulation was used as a standard basis of comparison in these tests due to its current wide use in the industry. In addition, compositions corresponding to those of the present invention but containing no enzymes were evaluated. The results of these tests presented in Table I conclusively show the outstanding performance advantages of the detergent compositions prepared according to this invention.

The wash-wear tests involved washing collars and cuffs from naturally soiled white dress shirts in the following manner. Shirts carrying detachable collars and cuffs were worn by male subjects under ordinary conditions for two normal working days. Following wearing, the collars and cuffs were washed for 10 minutes in a small agitator type machine using solutions of the detergent compositions to be evaluated. These washing solutions were prepared by adding to water of 7 grain hardness the various components of the compositions to be evaluated in the desired amounts. The washing conditions were as

herein specified in Table I. After four washing and drying cycles, the collars and cuffs were washed by a composition being evaluated were visually compared with similarly soiled collars and cuffs which were washed in the standard detergent composition under substantially the same conditions. The visual comparison was made by a group of five people who were familiar with the procedure and purpose of the test and formed their judgment independently.

The data from the visual judgments are expressed on a scale such that a value of 0 represents the cleaning ability of water alone and a value of 10.5 represents the cleaning ability of a very excellent detergent composition used under optimum laboratory conditions along with an effective bleaching agent. On this scale, a value of about 6.5 represents good, better than average, cleaning, while a value of about 3.5 represents unsatisfactory cleaning. The primary purpose of these determinations and this type of grading scheme was to establish the relative cleaning performance of several compositions of this invention in comparison with a commercially acceptable type of formula employing a linear alkylbenzene-sulfonate detergent and a sodium tripolyphosphate builder. The components and amounts of the materials employed in the washing solutions used in these white shirt detergency tests are indicated in Table I. In each instance sodium hydroxide was employed to adjust the pH of the solution to the stated value. No fluorescers, bleaches or anti-redeposition agents were employed, except where otherwise indicated, so as not to mask the cleaning effect of the compositions of the present invention. The washing solutions in each instance were standardized to the pH's indicated in Table I and in all instances the water used contained 7 grains per gallon of hardness. The temperatures of the washing solutions were indicated in Table I. The sodium linear alkylbenzenesulfonate employed as the anionic as the anionic active in the standardized detergent composition had an alkyl chain distribution averaging about 11.8.

This linear alkylbenzenesulfonate is indicated in Table I and II as LAS. The distribution of alkyl chains is as follows: C₁₀, 8.44; C₁₁, 33.59; C₁₂, 36.30; C₁₃, 16.02; C₁₄, 5.65.

TABLE I

(Solution Concentrations)
0.03% LAS; 0.06% sodium tripolyphosphate pH 10; 140°F.
(standard)

0.05% sodium β - acetoxylhexadecane - 1 - sulfonate; 0.04% citric acid; pH 7; 120°F.; 10 ppm Monsanto DA-10 enzyme

6.5 120

9.0

- 0.05% sodium β - acetoxyhexadecane - 1 - sulfonate; 0.04% citric acid; pH 7; 120°F. (no enzyme) 6.3
- 5 0.05% dimethylhexadecylammonio-propane sulfonate, 0.4% citric acid, pH 9, 120°F., 10 ppm Kikkoman Tp protease 9.2
- 10 For purposes of comparison with detergent compositions of the present invention and to illustrate the selectivity in the use of highly efficient organic detergents, the above-described wash-wear test was repeated employing a sodium linear alkylbenzenesulfonate described hereinbefore and sodium tallow-alkyl sulfate as the detergent actives. Sodium tripolyphosphate or citric acid was added as specified in Table II which describes the results of these tests.
- 20 **TABLE II**
Comparative Tests
(Solution Concentrations)
- 25 0.05% LAS; 0.06% sodium tripolyphosphate; pH 7; 120°F.; 10 ppm Monsanto DA-10 enzyme 5.7
- 0.05% sodium tallowalkyl-sulfate; 0.04% citric acid; pH 7; 120°F.; 5 ppm Pronase-E 4.8

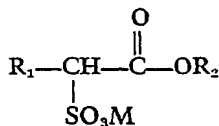
- 30 The results of Table I illustrate the superior cleaning properties of compositions of the present invention and illustrates the efficacy of each of these compositions in comparison with a standard alkaline built formulation commonly employed in the detergency industry and which compositions corresponding to those of the invention, but containing no enzymes. The results indicated in Table II illustrates the cleaning effects of compositions containing certain common anionic surfactants, builders and enzymes. These compositions fail to equal in cleaning performance the hereinbefore described standard composition or those of the present invention.
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- 40

45 WHAT WE CLAIM IS:—

1. A detergent composition comprising:

- A. from 10% to 85% by weight of a synthetic organic detergent or a mixture of detergents selected from the following:

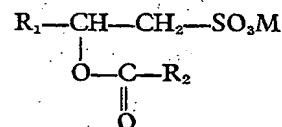
- 50 (i) compounds of the formula



where R_1 is alkyl or alkenyl having from 10 to 20 carbon atoms, R_2 is alkyl having from 1 to 10 carbon atoms and M is a salt-forming radical,

55

- (ii) compounds of the formula



where R_1 is alkyl having from 9 to 23 carbon atoms, R_2 is alkyl having from 1 to 8 carbon atoms and M is a salt-forming radical,

60

- (iii) compounds of the formula:

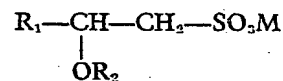


where R is alkyl or alkenyl having from 10 to 20 carbon atoms, x is within the range from 1 to 30 and M is a salt-forming radical,

65

- (iv) olefin sulphonates having from 12 to 24 carbon atoms,

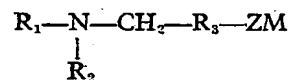
- (v) compounds of the formula



where R_1 is alkyl having from 8 to 20 carbon atoms, R_2 is alkyl having from 1 to 3 carbon atoms and M is a salt-forming radical,

70

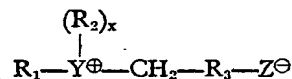
- (vi) compounds of the formula



where R_1 is alkyl having from 8 to 18 carbon atoms, R_2 is alkyl having from 1 to 3 carbon atoms or is hydrogen, R_3 is alkylene having from 1 to 4 carbon atoms, Z is carboxy, sulphonate or sulphate and M is a salt-forming radical,

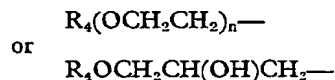
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- (vii) compounds of the formula



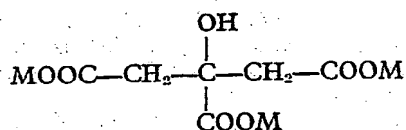
where R_1 is alkyl, alkenyl or hydroxyalkyl containing from 8 to 18 carbon atoms or a group

85



where R_4 is alkyl, alkenyl or hydroxyalkyl,

- n is 1—10 and R_1 has a total of 8—18 carbon atoms, Y is nitrogen, phosphorus or sulphur, R_2 is alkyl or monohydroxyalkyl having from 1 to 3 carbon atoms, x is 1 when Y is sulphur and 2 when Y is nitrogen or phosphorus, R_3 is alkylene or hydroxy alkylene having from 1 to 4 carbon atoms and Z is carboxylate, sulphonate, sulphate, phosphonate or phosphate; and
- 10 B. from 10% to 75% by weight of a citrate having the formula



- where M is hydrogen or a salt-forming radical; said composition having a pH within the range from 6 to 10 in aqueous solution at a concentration of 0.12% by weight.

2. A composition as claimed in claim 1, wherein there is also present from 0.001% to 5% by weight of a proteolytic enzyme having a proteolytic activity in aqueous solution at temperatures of up to 130°F.

3. A composition as claimed in claim 2, wherein from 0.01% to 1% of the enzyme is present.

4. A composition as claimed in claims 2 or 3, wherein the proteolytic enzyme is a bacterial, fungal or mould protease.

5. A composition as claimed in claim 4, wherein the protease is trypsin, collagenase, keratinase, elastase, subtilisin, BPN or BPN'.

6. A composition as claimed in claim 4 or 5, wherein the proteolytic enzyme is used in the form of a powdered composition comprising from 2% to 80% by weight of protease and from 20% to 98% by weight of a powdered material selected from inorganic alkali metal salts, inorganic alkaline earth metal salts, non-enzymatic proteins, carbohydrates, organic clays, starches, lipids and mixtures thereof.

7. A composition as claimed in claim 6, wherein the powdered composition is employed in an amount within the range from 0.03% to 10% by weight based on the total detergent composition.

8. A composition as claimed in claim 7, wherein the powdered composition is employed in an amount within the range from 0.1% to 5% by weight.

9. A composition as claimed in any one of claims 1 to 8, wherein the synthetic organic detergent is present in an amount within the range from 15% to 50% by weight of the total composition.

10. A composition as claimed in any one of claims 1 to 9, wherein the synthetic organic detergent has formula (ii) given in claim 1 in which R_1 is alkyl having from 12 to 16 carbon atoms, R_2 is methyl and M is alkali metal.

11. A composition as claimed in any of claims 1 to 8, wherein the synthetic organic detergent has formula (iii) given in claim 1 in which R is tallow alkyl, x is within the range from 1 to 6 and M is alkali metal.

12. A composition as claimed in any one of claims 1 to 9, wherein the synthetic organic detergent is alkali metal olefin sulphonate having from 12 to 24 carbon atoms.

13. A composition as claimed in any one of claims 1 to 9, wherein the synthetic organic detergent has formula (vii) given in claim 1 in which R_1 is alkyl having 16 carbon atoms, R_2 is methyl, x is 2, Y is nitrogen, R_3 is propylene and Z is sulphonate.

14. A composition as claimed in any one of claims 1 to 13, wherein component B is a citrate of the formula given in claim 1, wherein M is alkali metal, ammonium, or substituted ammonium.

15. A composition as claimed in any one of claims 1 to 14, wherein there is also present an inorganic salt or other phosphate-free builder.

16. A composition as claimed in any one of claims 1 to 15, wherein there is also present a minor amount of one or more of the following ingredients: a soil redeposition inhibitor, a tarnish inhibitor, a fluorescer, perfume, colour, water, other enzymes, a brightening agent and a bleaching agent.

17. A detergent composition substantially as described herein with reference to the Examples.

18. A method of laundering textile materials, which comprises treating them with a composition as claimed in any one of claims 1 to 17.

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